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SO₂ capture and detection with carbon microfibers (CMFs) synthesised from polyacrylonitrile†

Ana Yañez-Aulestia, 📵 a Valeria B. López-Cervantes, 📵 b J. Marcos Esparza-Schulz, a Diego Solis-Ibarra, 📵 b Ilich A. Ibarra, 🗓 bc Salomón Cordero-Sánchez, * 5 Elí Sánchez-González * and Reyna Ojeda-López*

SO₂ emissions not only affect local air quality but can also contribute to other environmental issues. Developing low-cost and robust adsorbents with high uptake and selectivity is needed to reduce SO2 emissions. Here, we show the SO₂ adsorption-desorption capacity of carbon microfibers (CMFs) at 298 K. CMFs showed a reversible SO₂ uptake capacity (5 mmol g⁻¹), cyclability over ten adsorption cycles with fast kinetics and good selectivity towards SO2/CO2 at lowpressure values. Additionally, CMFs' photoluminescence response to SO₂ and CO₂ was evaluated.

Sulphur dioxide (SO₂) is a highly toxic gas that is accountable for severe respiratory illnesses, even at very low concentrations. For example, exposure to small amounts of SO₂ (as low as 1.5 ppm) for only a few minutes can cause momentary incapacity to breathe, and at higher concentrations (above 100 ppm) can cause death.1

Different strategies to remove SO2 (flue gas desulphurisation processes FGD) have been typically used with acceptable results. These include limestone scrubbers (producing calcium sulphite)² and even SO₂ fixation (disulfitomercurate).³ However, these procedures exhibited drawbacks associated with large amounts of wastewater, high toxicity, corrosion of pipelines, and high recuperation fees. Other SO₂ capture alternatives, such as silicas, zeolites, metal oxides, and activated carbons, have exhibited low SO₂ efficiency.^{4,5} Although metalorganic frameworks (MOFs) have demonstrated promising SO₂ capture results, for example, MOF-177 and MIL-101(Cr) showing high SO₂ capture values, the crystal structure of these materials collapsed after being in contact with SO₂.6

Most of the current research on SO2 has been narrowly focused on capturing this corrosive gas. However, the SO2 capture is not the only relevant; SO2 detection is as suitable as the capture and conversion of SO₂. Efficient materials for SO₂ detection are required to comply with the following characteristics: (i) high chemical stability towards SO2 under more realistic conditions (60% of relative humidity), (ii) nondependency on relatively high surface areas, and (iii) high processability.6 In addition to remarkable chemical and structural stability, such "detector materials" are characterised for showing high SO₂ uptake at low pressure, providing feasible applicability in SO₂ detection devices.8 Cooper et al. demonstrated outstanding SO₂ capture in porous organic cages (POCs) at low pressure. 9,10 Therefore, new porous platforms have appeared as exciting alternatives to capture and detect corrosive and explosive gases. For example, Hiraoka and co-workers reported a functionalised organic nanotube with optimal selective fluorescence properties to detect liquefied petroleum gas.¹¹

Carbon materials have been explored for SO₂ capture. Yi et al., tested coconut shell-based activated carbon (SAC) and coal-based activated carbon (CAC), where SAC was the best adsorbent for SO₂. 12 Muñiz et al. performed thermal and chemical treatments to enhance the SO2 uptake on activated carbon fibres, and they concluded that the superficial functionalities with a basic character seem to be the most important characteristic concerning SO₂ capture. ¹³ Wang et al., developed a series of N-doped coal-based porous carbons (NCPCs) by calcining a mixture of anthracite, MgO, KOH and carbamide at 1073 K; their results showed that the balance between nitrogen doping content and specific surface area (microporosity) improved the number of active adsorption sites of SO₂. 14 In this context, the carbon microfibers (CMFs) obtained

^a Laboratorio de Fisicoauímica de Superficies. Departamento de Ouímica. Universidad Autónoma Metropolitana-Iztapalapa (UAM-I), Mexico City, CDMX 09310. Mexico. E-mail: scs@xanum.uam.mx. rol@xanum.uam.mx

^b Laboratorio de Fisicoquímica y Reactividad de Superficies (LaFReS), Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior s/n, CU, Del Coyoacán, 04510, Ciudad de México, Mexico. E-mail: elis@materiales.unam.mx

^c On sabbatical as "Catedra Dr Douglas Hugh Everett" at Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, San Rafael Atlixco 186, Col. Leyes de Reforma 1ra Seccion, Iztapalapa, C.P. 09310, Ciudad de México, Mexico

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by calcination of polyacrylonitrile microfibers (PANMFs)¹⁵ present an opportunity for SO2 detection due to the following aspects: (i) chemical composition based on nitrogen and oxygen functional groups resulting from the polymer precursor (PAN), (ii) high microporosity controllable depending on calcination temperature, (iii) good thermal stability, and (iv) reversible gas adsorption (e.g., CO2 or CH4). Concerning nitrogen functional groups, there have been identified four groups in the CMFs: N-6 (pyridine-N), N-5 (pyrrolic-N), N-X (pyridine-N-oxide) and N-Q (quaternary-N or graphitic-N). 15 Some of these groups have improved the performance of CMFs in oxygen reduction reactions (ORR) in fuel cells16 and their gas adsorption properties (CO₂ and CH₄).¹⁵

Textural, chemical, and structural characterisation of the CMFs have been reported previously (Fig. S1, ESI†). To CMFs were obtained by calcination of PANMFs at 1173 K; this material has a specific surface area of 731 m² g⁻¹, a total pore volume of $0.348 \text{ cm}^3 \text{ g}^{-1}$, and a microporosity above 70%. An average pore size of 0.78 nm was calculated from the N₂ adsorption isotherm at 77 K, and 0.5 nm was estimated using the CO₂ adsorption isotherm at 273 K.¹⁷ The CMFs average chemical composition is C: 89%, N: 6%, and O: 5%. It is important to mention that the fibrous structure of PANMFs is preserved after calcination with fibre diameters between 200 and 400 nm.

Since CMFs contain several nitrogen sites, which can be potential SO₂-adsorption sites, we measured the SO₂ adsorption

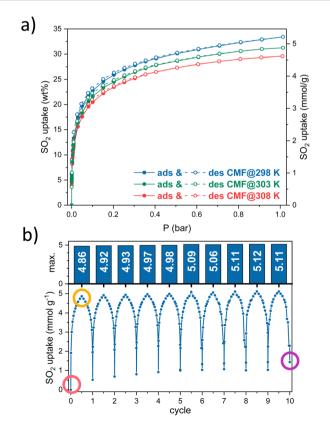


Fig. 1 (a) SO₂ adsorption-desorption isotherms at 298, 303, and 308 K, (b) ten SO₂ adsorption-desorption cycles on CMFs.

at 298, 303 and 308 K (Fig. 1a). SO2 isotherms showed a type-I profile based on IUPAC18 with a small hysteresis. CMFs showed a maximum uptake of 5.2, 4.9 and 4.6 mmol g⁻¹ at 1 bar for 298, 303 and 308 K, respectively. This value is higher than several reported in the literature compared to other carbonaceous or inorganic materials in the function of superficial area BET (Fig. S4, ESI†). The three SO2 adsorption isotherms were used to calculate the isosteric enthalpy of adsorption, obtaining values around $-30 \text{ kJ} \text{ mol}^{-1}$ (see Fig. S3, ESI†), consistent with a physisorption process and mild regeneration conditions.

Then, cyclability tests were carried out to evaluate the reusability of the material at the conditions where the highest SO₂ capture was obtained. Ten SO₂ adsorption-desorption cycles were performed at 298 K until 1 bar. The amount of SO_2 captured in each cycle is stable, around 5 mmol g^{-1} (Fig. 1b). Between each cycle, a vacuum activation process was enough to desorb almost all the SO2 adsorbed, leading to the slight increase in the baseline and thus, the maximum SO₂ uptake in each cycle.

FTIR-ATR and SEM measurements were performed to characterise the CMFs in the SO₂ capture process (Fig. 2). In the three different stages during the SO2 uptake (before and after the first adsorption cycle and after ten desorption cycles indicated by pink, yellow and purple colours, respectively, in Fig. 1 and 2), the IR-ATR spectra showed the presence of ester groups between 2250 to 2000 cm⁻¹, and coupling C-N stretching and N-H deformation modes of C-N-H groups (amide)

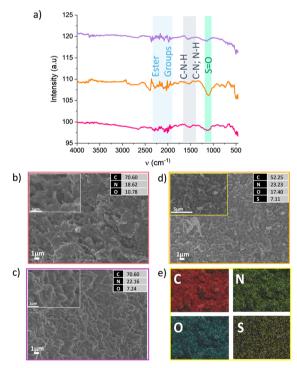


Fig. 2 (a) IR-ATR spectra at different stages according to the points marked in Fig. 1b, pristine sample (pink), after SO₂ uptake (yellow), and after 10 desorption cycles (violet). SEM micrographs with their EDX results on (b) pristine sample, (c) after 10 desorption cycles, (d) after SO₂ uptake, and (e) the EDX mapping results of the rectangular area inside panel (d).

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a)

around 1522 cm⁻¹. For the SO₂-saturated CMFs sample, a characteristic band in 1050 cm⁻¹ was identified, indicating the S=O group was present (Fig. 2a). 19,20 These results are in good agreement with the SEM micrographs and EDX analyses. Carbon microfibres morphology only changes when the SO₂ capture process occurs; the surface showed small globularities protruding from the fibre channels, and the EDX results showed sulphur presence of around 7 wt% and an increment of the oxygen percentage as well (Fig. 2d). The EDX mapping displayed a homogeneous distribution of C, N, O and S on the surface in the area shown inside the 5 µm scale micrograph in Fig. 2d. The sample showed the same morphology and composition before starting the cycles (Fig. 2b), with the sample pristine and after the last desorption cycle (Fig. 2c). These results indicate that the CMFs are stable against SO2 for ten adsorption-desorption cycles.

Considering that SO₂ is often found as a minor component of flue gas mixtures (diluted in CO₂ and/or N₂), the separation selectivity is a crucial factor to consider. The SO₂/CO₂ separation selectivity was determined employing the ideal adsorbed solution theory (IAST) using two monocomponent isotherms of SO₂ and CO₂ at 298 K (Fig. 3a, details on ESI†). The CMFs exhibited good selectivity values for the binary mixtures SO₂/CO₂ in the low-pressure domain, 122, 118 and 110 for

1%, 5% and 10% of SO₂ at 0.05 bar, respectively (Fig. 3b). The IAST selectivity result is comparable with similar superficial area BET adsorbents such as zeolite Y (180, 930 m² g⁻¹),²¹ Mggallate (321, 576 m² g⁻¹),²² Co-gallate (143, 494 m² g⁻¹),²² DMOF-TM (169, 900 m² g⁻¹),²³ MIL-160 (128, 1170 m² g⁻¹),²⁴ Cu-ATC (114, 600 m 2 g $^{-1}$), 25 NbOFFIVE-Cu-TPA (78, 1179 m 2 g $^{-1}$), 26 Granted, the SO₂ uptake of CMFs falls short in front of benchmark materials. However, these results invite us to explore another application of the CMFs, SO₂ detection, where the reversible adsorption and selectivity are relevant.

Photoluminescence experiments were carried out on the CMFs using a λ_{ex} = 370 nm after exposure to an SO₂-saturated atmosphere (details on ESI†). The PL intensity increased by about 50% after the SO₂ exposure, compared to the activated sample (Fig. 4a). This switch-on emission decreased over time: after 15 min of exposure, the emission returned to the value of the reference sample. However, when the sample is not activated and has been left in contact with the environment, the signal increases, indicating that it detects other molecules, such as H₂O or CO₂. To evaluate this hypothesis, PL measurements were performed by saturating the CMFs with CO₂ and H₂O separately (Fig. S6, ESI†). The results showed a positive response for carbon dioxide but not for water. The presence of specific functional groups on carbon materials as the nitrogen-

> SO_a saturated CMFs As synthesised CMFs

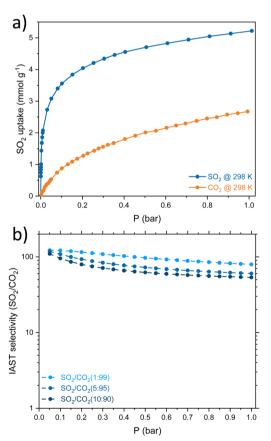


Fig. 3 $\,$ (a) Comparison of the SO_2 and CO_2 adsorption isotherms at 298 K on CMFs. (b) IAST selectivity of SO₂/CO₂ on MCFs for different concentrations of the binary mixture.

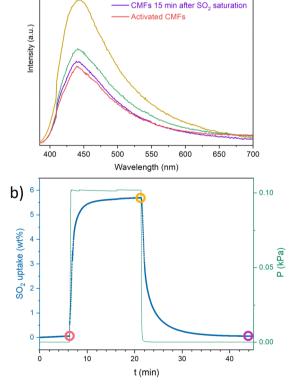


Fig. 4 (a) Photoluminescence CMFs spectra (λ_{ex} = 370 nm) of as synthesised, activated, SO₂ saturated and after the exposure to SO₂ samples. (b) Profile of adsorption-desorption kinetics of SO₂ on CMFs (gravimetric experiment with controlled SO₂ atmosphere).

bearing active sites in the CMFs (in the form of NH₂, for example, where nitrogen acts as an electron donor) may enhance the interaction with SO2 and the resulting photoluminescent response. The interaction between these gases with free electron pairs favours light absorption and subsequent emission for detection.²⁷ For the SO₂ interaction, the observed reversibility agrees with the observed adsorption-desorption kinetics of SO₂ obtained by gravimetric experiments (Fig. 4b).

However, even though a similar PL intensity was observed for

CO₂ exposed sample compared to SO₂, the PL emission of the

CO₂ exposed sample remained after several hours, indicating a

slow desorption of this gas molecule (Fig. S7, ESI†).

In summary, SO₂ adsorption-desorption capacity at room temperature and 1 bar of CMFs was around 5 g mol⁻¹. It maintained good chemical and morphological stability during 10 adsorption-desorption cycles of SO₂ and a good SO₂/CO₂ selectivity, achieving a reasonable degree of reuse. When evaluating the photoluminescence of the material, it was determined that it can detect SO₂ and CO₂ but not H₂O and that SO₂ desorption is faster than CO2. CMFs may be functionalised to improve their textural properties, SO₂ uptake and selectivity overall.

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Conflicts of interest

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There are no conflicts to declare.

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